En Chem, Inc.

Quality Assurance Document

SET No: 1

ANALYTICAL METHOD

TITLE: Hardness by Calculation

DEPARTMENT: Inorganic - Metals

APPLICATION: Determination of total hardness in an aqueous matrix.

REFERENCE: Standard Methods 2340 B., 17th Edition, 1989

PROCEDURE SUMMARY:

To conform with current practices, hardness is defined as the sum of calcium and magnesium ions expressed as calcium carbonate in milligrams per liter. Aqueous samples are prepared using appropriate analytical digestion procedures. Calcium and magnesium concentrations are determined by Inductively Coupled Argon Plasma. Hardness by calculation is applicable to all water matrices.

REPORTING LIMIT:

5.0 mg/L

REVIEWED BY: _____ 4-13-00
Jeffrey A. Gordon — Date
Inorganic Section Supervisor

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Quality Assurance Officer

APPROVED BY: _____ 4-14-00
Glen A. Coder — Date
Laboratory Manager

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SAMPLE HANDLING AND PRESERVATION:

Samples are preserved by adding concentrated nitric acid (HNO_3) to obtain a pH <2. Once preserved, the sample holding time may not exceed 6 months. Samples can be collected in glass or plastic containers.

INTERFERENCES:

Interferences encountered using Inductively Coupled Plasma at the wavelengths chosen for calcium and magnesium analyses should be examined (See Method MET-27, Inductively Coupled Plasma Atomic Emission Spectroscopy, Or MET-58 ICPMS for Interferences).

APPARATUS AND MATERIALS:

Thermo-Jarrell Ash, 61E Trace Inductively Coupled Argon Plasma Spectrophotometer. Or Hewlett Packard 4500 ICPMS (See Method MET-2: Acid Digestion of Aqueous Samples for Dissolved or Total Recoverable Metals - ICP, and MET-3: Acid Digestion of Aqueous Samples for Total Metals - ICP, MET-45: Microwave Digestion-Aqueous, Apparatus and Materials: See Method MET-58 or MET-42, Apparatus.)

REAGENTS AND STANDARDS:

See Methods MET-2, MET-3, MET-45, Reagents. See Method MET-27 or MET-58, Reagents.

SAMPLE PREPARATION:

Samples are prepared using EN CHEM analytical digestion methods. For ground water and total recoverable metals, see Method MET-2 or MET-45; for aqueous total metals, see Method MET-3 or MET-45.

INSTRUMENT OPERATION:

See Method MET-27, MET-58, or MET 42, for operation of instrument and determination of the calcium and magnesium concentrations (Concentration Units: mg/L).

QUALITY CONTROL:

Initial Calibration Verification (ICV)
The ICV must be analyzed immediately after calibration and meet the rejection criteria of $\pm$10% of the true value. Recalibrate if the ICV fails. The concentration of the ICV should be near the mid-point of the calibration curve.

Initial Calibration Blank (ICB)
The ICB must be analyzed after the ICV. The absolute value must be ≤3xIDL. Recalibrate if it fails. However, if the ICB concentration is <1/10 the concentration of the associated samples, the analysis need not be terminated.

Continuing Calibration Verification (CCV)
The CCV is analyzed after every 10 samples. Rejection criteria is ±10% of true value. If the CCV fails, the problem must be corrected and the previous 10 samples between the CCV and last CCB must be reanalyzed. Concentration of the CCV should be near the mid-point of the calibration curve. For ICP analysis, as long as the CCV's that bracket the samples to be reported for the analytes of interest are within the acceptable limit, then the run is acceptable.

Continuing Calibration Blank (CCB)
The CCB is analyzed after every CCV. The absolute value must be ≤ 3xIDL. If the CCB fails, the problem must be corrected and the previous 10 samples between the last CCB and the CCV must be reanalyzed. However, if the CCB concentration is < 1/10 the concentration of the associated samples, then those samples need not be reanlalyzed.

Laboratory Control Sample (LCS)
The LCS is carried through all preparation procedures and analyzed for each matrix type with a frequency of 5%. See current QC Charts for control ranges. In cases where the LCS is outside of acceptable ranges all samples prepared in that batch must be reprepared and reanalyzed.

Method Blank (MB)
A MB is carried through all prep procedures and analyzed with a frequency of 5%. Rejection criteria is <LOD. Other criteria may apply, such as regulatory limit and the analyte concentration in the samples.

Serial Dilution Test (For ICP analysis)
A Serial Dilution Test is performed if the analyte concentration is sufficiently high(50X the EQL). For these samples a 1:5 dilution is performed and the result should agree within ± 10% of the original value. If the results do not agree the data is flagged with an [E flag.

Batch Post Spike (For ICP analysis)
A Batch Post Spike is required at a frequency of 5%. The control limits for a post-spike are 75-125%. If the post-spike recovery is out-of-control, dilute the corresponding sample and perform a post-spike on the diluted aliquot of sample. Dilute appropriately until an acceptable recovery is obtained.

ICSA / ICSAB (For ICP analysis)
There is no criteria established for the ICSA; however, the analyst should be aware that if the result is greater than ± EQL, the IEC's made need adjustment.

The criteria for the recoveries on the ICSAB are 80-120%. There is no criteria on the minerals or for Fe or Al, as these elements are used as the interferent.

ACCURACY

One matrix spike and matrix spike duplicate are analyzed for each group of samples that are similar in matrix at a frequency of 5%. Both QC samples must be calculated for accuracy. See current QC charts for control range.

$$\text{Spike Percent Recovery} = \frac{SSR - SR}{SA}$$

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

If both spike recoveries are outside of the specified control limit, the corresponding parent sample is to be post-spiked and the reported result shall be flagged with a [N qualifier. The control limits for a post-spike are 75-125%. If the post-spike recovery is out-of-control, dilute the corresponding sample and perform a post-spike on the diluted aliquot of sample. Dilute appropriately until an acceptable recovery is obtained. If only the matrix spike OR the matrix spike duplicate are out of control for accuracy, then the corresponding parent sample is flagged with a [MS qualifier.

If the analyte of interest is greater than the linear range, dilute appropriately and post-spike the sample; however, a [N qualifier is not required. Also, if the analyte of interest is greater than 4x the level of the spike concentration, accuracy calculations are not necessary.

If there is insufficient sample volume to perform a matrix spike and a matrix spike duplicate a LCS and an LCS DUP must be used in its place.

PRECISION

Matrix spike duplicate samples are analyzed 1 per batch or at a frequency of 5%, for samples that are similar in matrix.

For matrix spike duplicate samples, relative percent difference (RPD) is used to calculate compliance. See current QC charts for control limits.

Calculation:

$$RPD = \frac{MS - MSD}{(MS+MSD)/2} \times 100$$

MS = Method Spike Value
MSD = Method Spike Duplicate Value

If the RPD is outside of the acceptable control limits, the reported sample result is to be qualified with an [* flag.

Sample Result Calculations:

Milligram equivalent Ca_2CO_3/L (Hardness) = 2.497[Ca, mg/L] + 4.118[Mg, mg/L]

IF METHOD EPA 200.7 IS REQUESTED

A matrix spike addition of 20-100x the MDL should result in 90-110% recovery or be within the established control limits.

Store calibration standards in plastic.

Samples which were preserved in house must be held for 16 hours prior to analysis.

ICV/CCV control limits are 95-105%

If digestion is required: 1 LRB per batch at the time of analysis.
1 LFB per batch at the time of analysis.

Perform a matrix spike at a minimum of 10% of the samples or one per sample batch, whichever is greater.

SAFETY:

The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Laboratory staff should observe all safety procedures as outlined in the Laboratory Health and Safety Manual. Staff should consult Materials Safety Data Sheets (MSDS) for information on specific chemicals.

POLLUTION PREVENTION and WASTE MANAGEMENT:

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Laboratory staff should order and prepare only those quantities of reagents that will be used prior to the expiration date. Other appropriate measures to minimize waste generation should be brought to the attention of laboratory management. All laboratory waste shall be handled as directed by the Laboratory Waste Management Plan and Hazardous Waste Contingency Plan.